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1. REPORT DATE (DD-MM-YYYY) 16-03-2006		2. REPORT TYPE Journal Article		3. DATES COVERED (From - To)	
4. TITLE AND SUBTITLE  Preparation , Characterization, and Crystal Structures of the SO <sub>3</sub> NHF <sup>-</sup> and SO <sub>3</sub> NF <sub>2</sub> <sup>-</sup> Anions (PREPRINT)			5a. CONTRACT NUMBER		
			5b. GRANT NUMBER		
			5c. PROGRAM ELEMENT NUMBER		
6. AUTHOR(S) Ralf Haiges, Ross Wagner, Muhammed Yousufuddin, Markus Etzkorn, G.K. Surya Prakash, & Karl O. Christe (USC); Jerry A. Boatz (AFRL/PRSP); Robert D. Chapman (NAWC); Mark F. Welker & Charles B. Kreutzberger (TPL, Inc.)			5d. PROJECT NUMBER		
			5e. TASK NUMBER 23030423		
			5f. WORK UNIT NUMBER		
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)  Air Force Research Laboratory (AFMC) AFRL/PRSP 10 E. Saturn Blvd. Edwards AFB CA 93524-7680			8. PERFORMING ORGANIZATION REPORT NUMBER  AFRL-PR-ED-JA-2006-101		
9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)  Air Force Research Laboratory (AFMC) AFRL/PRS 5 Pollux Drive Edwards AFB CA 93524-7048			10. SPONSOR/MONITOR'S ACRONYM(S)		
			11. SPONSOR/MONITOR'S NUMBER(S) AFRL-PR-ED-JA-2006-101		
12. DISTRIBUTION / AVAILABILITY STATEMENT  Approved for public release; distribution unlimited (AFRL-ERS-PAS-2006-084)					
13. SUPPLEMENTARY NOTES Submitted to Angewandte Chemie.					
14. ABSTRACT Recently, a new class of high-energy-containing materials, <i>gem</i> -bis(difluoramino)-substituted heterocyclic nitramines, has gained attention as high-energy oxidizers: HNF <sup>1,2</sup> and TNF <sup>3</sup> have been successfully synthesized under strongly acidic conditions from their corresponding ketone derivatives using an excess of difluoramine. <sup>4</sup> HNF <sub>2</sub> is an unpredictably shock-sensitive and thermally unstable, gaseous compound <sup>5,6</sup> which can be generated from different precursors, e.g., tetrafluorohydrazine, <sup>7</sup> <i>N,N</i> -difluorourea, <sup>8</sup> <i>N,N</i> -difluorocarbamates, <sup>9</sup> or trityldifluoramine. <sup>10</sup> Out of these precursors, only trityldifluoramine is a stable storable solid. However, it is not useful as a general reagent for the preparation of larger quantities of <i>gem</i> -bis(difluoramines) because its synthesis requires the use of expensive N <sub>2</sub> F <sub>4</sub> which is commercially unavailable and must be prepared from difluoramine, and of equivalent amounts of mercury in an organic solvent. The use of mercury presents environmental problems, and working with N <sub>2</sub> F <sub>4</sub> in an organic solvent can be hazardous. Therefore, it is highly desirable to develop a stable, solid, readily accessible difluoramine source. Obvious candidates for HNF <sub>2</sub> sources were difluorosulfamate salts. Although the parent free acid, HOSO <sub>2</sub> NF <sub>2</sub> , had been known since 1961 and has been widely used as a difluoroaminating reagent, <sup>11,12</sup> no reports could be found on the existence of its salts. In this paper, we report the results from two independent studies.					
15. SUBJECT TERMS					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT	b. ABSTRACT	c. THIS PAGE			Dr. Scott A. Shackelford
Unclassified	Unclassified	Unclassified	A	29	19b. TELEPHONE NUMBER (include area code) N/A

((Subject Heading))

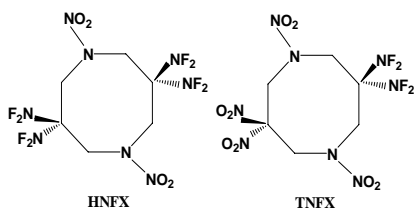
DOI: 10.1002/anie.200123456

## Preparation, Characterization, and Crystal Structures of the $\text{SO}_3\text{NHF}^-$ and $\text{SO}_3\text{NF}_2^-$ Anions\*\*

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Dedicated to Dr. Carl Schack on the occasion of his 70<sup>th</sup> birthday

Recently, a new class of high-energy-containing materials, *gem*-bis(difluoramino)-substituted heterocyclic nitramines, has gained attention as high-energy oxidizers:  $\text{HNFX}^{[1,2]}$  and  $\text{TNFX}^{[3]}$  have been successfully synthesized under strongly acidic conditions from their corresponding ketone derivatives using an excess of difluoramine.<sup>[4]</sup>



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[\*\*] The work at USC was funded by the Air Force Office of Scientific Research, the Office of Naval Research, Lawrence Livermore National Laboratory, and the National Science Foundation, and that at NAWCWD and TPL, Inc. was supported by the Office of Naval Research. Portions of this work were previously reported in limited-distribution presentations.<sup>[1]</sup> Supporting information for this article is available on the WWW under <http://www.angewandte.org> or from the author.

$\text{HNF}_2$  is an unpredictably shock-sensitive and thermally unstable, gaseous compound<sup>[5,6]</sup> which can be generated from different precursors, e.g., tetrafluorohydrazine,<sup>[7]</sup> *N,N*-difluorourea,<sup>[8]</sup> *N,N*-difluorocarbamates,<sup>[9]</sup> or trityldifluoramine.<sup>[10]</sup> Out of these precursors, only trityldifluoramine is a stable storable solid. However, it is not useful as a general reagent for the preparation of larger quantities of *gem*-bis(difluoramines) because its synthesis requires the use of expensive  $\text{N}_2\text{F}_4$  which is commercially unavailable and must be prepared from difluoramine, and of equivalent amounts of mercury in an organic solvent. The use of mercury presents environmental problems, and working with  $\text{N}_2\text{F}_4$  in an organic solvent can be hazardous. Therefore, it is highly desirable to develop a stable, solid, readily accessible difluoramine source. Obvious candidates for  $\text{HNF}_2$  sources were difluorosulfamate salts. Although the parent free acid,  $\text{HOSO}_2\text{NF}_2$ , had been known since 1961 and has been widely used as a difluoroaminating reagent,<sup>[11,12]</sup> no reports could be found on the existence of its salts. In this paper, we report the results from two independent studies.

At TPL, Inc.,  $\text{Na}^+\text{SO}_3\text{NF}_2^-$  was first isolated by fluorinating aqueous sulfamic acid at 0 °C, neutralizing the product with concentrated aqueous sodium hydroxide, filtering off the less-soluble sodium fluoride by-product, and drying the neutral solution under vacuum. This process was improved by utilizing aqueous sodium sulfamate as a reactant, which is even more soluble than sulfamic acid. This modification required removal of less water for isolation. Maintaining neutral or slightly basic conditions with added sodium hydroxide or sodium carbonate during the aqueous fluorination proved beneficial, as the stability of acidic difluorosulfamic acid is poorer than that of neutral salt solutions. Sodium difluorosulfamate of ~96% purity could be prepared in this manner.

After storage in a refrigerator at ~0 °C for one month, solid sodium difluorosulfamate that was prepared in this way showed signs of degradation, as evidenced by its  $^{19}\text{F}$  NMR spectrum in  $\text{D}_2\text{O}$ . However, dilute aqueous solutions maintained at pH 7–8 (with dilute aqueous  $\text{NaHCO}_3$ ) appeared to be stable for several weeks at room temperature, according to  $^{19}\text{F}$  NMR, and, after 64 days at room temperature, only slight changes were apparent. After nine years, one such sample showed no residual difluorosulfamate content.

At USC, the synthesis of the  $\text{SO}_3\text{NF}_2^-$  and  $\text{SO}_3\text{NHF}^-$  anions was achieved by direct fluorination of  $\text{SO}_3\text{NH}_2^-$  salts with diluted elemental fluorine in unbuffered aqueous solutions at 0 °C [Eq. (1)].



The reaction conditions were similar to those previously used successfully for the fluorination of urea,<sup>[8a]</sup> carbamates<sup>[9a]</sup> and sulfamide.<sup>[13]</sup> The acidic reaction mixture was not stable above ~5 °C, and fast hydrolysis of the difluorosulfamate [Eq. 2] occurred upon warming to ambient temperature.



The ease of this acid-catalyzed hydrolysis can account for the lack of previous reports to isolate salts of the difluorosulfamate anion. The successful isolation of difluorosulfamate salts required careful control of the reaction conditions and rapid removal of the water and HF by-product at 0 °C in a vacuum. This method resulted in the isolation of pure, colorless  $\text{NaSO}_3\text{NF}_2$  in 94% yield. The dry sodium salt is stable at room temperature but decomposes when exposed to atmospheric moisture. It was stored in the dry argon atmosphere of a glove box for a period of 4 months without showing any sign of decomposition. The identity of the compound was established by the observed material balance, vibrational and

multinuclear NMR spectroscopy, electronic structure calculations, and by converting it into  $[\text{PNP}][\text{SO}_3\text{NF}_2]\cdot\text{CH}_2\text{Cl}_2$  (PNP = bis-(triphenylphosphoranylidene)ammonium) and determining its crystal structure.

The observed Raman and IR spectra of solid  $\text{NaSO}_3\text{NF}_2$  are shown in Figure 1, and the observed frequencies and intensities are listed in Table 1. They were assigned by comparison with those calculated at the MP2<sup>[14]</sup> level of theory using the 6-311+G(d) basis set.

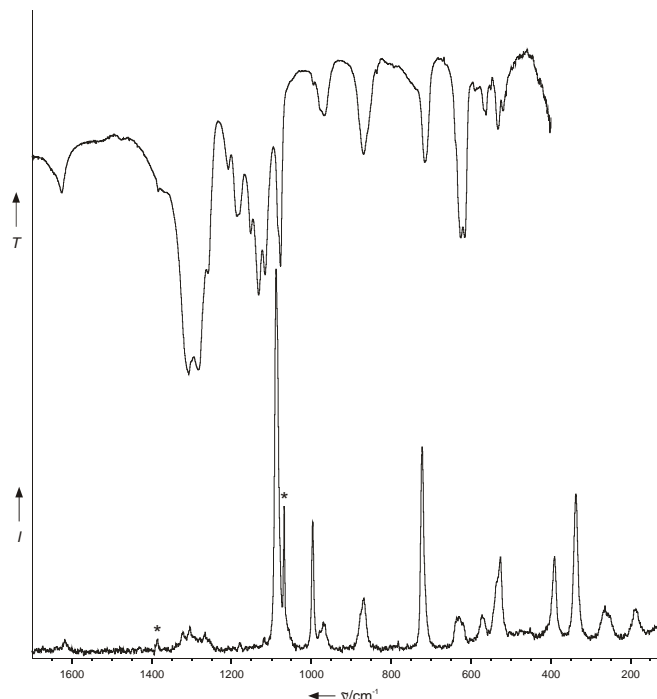
**Table 1.** Comparison of observed and unscaled calculated MP2/6-311+G(d) vibrational frequencies ( $\text{cm}^{-1}$ ) and intensities for  $\text{SO}_3\text{NF}_2^-$  in point group  $C_s$ .

mode		approx. mode description in point group $C_s$	observed <sup>[a],[e]</sup>		calculated <sup>[b]</sup>
			IR	Raman	
a'	$\nu_1$	$\nu_{\text{as}} \text{SO}_3$	1309	1304	1286 (364)
			vs	[0.8]	[7.2 dp]
	$\nu_2$	$\nu_s \text{SO}_3$	1080 s	1089	1051 (59)
				[10.0]	[38 p]
	$\nu_3$	$\nu_s \text{NF}_2$	968 w	997	979 (72)
				[4.0]	[4.4 p]
				971	
				[0.9]	
a''	$\nu_4$	$\nu \text{SN}$	715 m	722	671 (64)
				[5.5]	[17 p]
	$\nu_5$	$\delta_{\text{sciss}} \text{SO}_2$	627 s	630	601 (140)
			617 s	[1.1]	[0.6 dp]
	$\nu_6$	$\delta_{\text{umbrella}} \text{SO}_2$		526	521 (1.6)
				[2.6]	[7.3 p]
	$\nu_7$	$\delta_{\text{sciss}} \text{NF}_2$	525 vw		501 (25)
					[4.6 p]
a''	$\nu_{10}$	$\nu_{\text{as}} \text{SO}_3$	1284	1267	1282 (362)
			vs	[0.7]	[7.7 dp]
	$\nu_{11}$	$\nu_{\text{as}} \text{NF}_2$	869 m	868	829 (75)
				[1.6]	[2.1 dp]
	$\nu_{12}$	$\delta_{\text{sciss}} \text{SO}_2$	532 w	537	532 (35)
				[2.0]	[3.5 dp]
	$\nu_{13}$	$\delta_{\text{rock}} \text{SO}_2$		390	325 (0.8)
				[2.6]	[0.8 dp]
	$\nu_{14}$	$\delta_{\text{wag}} \text{NF}_2$		186	154 (0.02)
				[1.3]	[6.1 dp]
a''	$\nu_{15}$	$\tau \text{SN}$		37	37 (0.00)
				[d]	[2.0 dp]

[a] As  $\text{Na}^+$  salt. Relative IR and Raman intensities given in parentheses and brackets, respectively. [b] IR intensities given in  $\text{km mol}^{-1}$  and Raman intensities given in  $\text{\AA}^4 \text{amu}^{-1}$ . [c] Not observed, IR spectrum recorded only between 4000 and  $400 \text{ cm}^{-1}$ . [d] Not observed, Raman spectrum recorded only between 3600 and  $80 \text{ cm}^{-1}$ . [e] In addition to the listed bands, IR bands at 1627 m, 1209 w, 1184 m, 565 w, and Raman bands at 1618 [0.5], 1321 [0.7], 572 [1.2]  $\text{cm}^{-1}$  were observed which were not assigned.

While the  $^{19}\text{F}$  NMR spectrum of naturally abundant  $^{14}\text{N}[\text{NaSO}_3\text{NF}_2]$  in  $\text{CD}_3\text{CN}$  gives only a broad resonance at  $\delta = 34$  ppm, the spectrum of an  $^{15}\text{N}$ -labeled sample in the same solvent shows a sharp doublet at  $\delta = 33.8$  ppm with  $^1J(^{19}\text{F}-^{15}\text{N}) = 138$  Hz. In the  $^{15}\text{N}$  NMR spectrum of the sample, a sharp triplet at  $\delta = -20.4$  ppm with the same  $^1J(^{15}\text{N}-^{19}\text{F})$  coupling constant was observed.

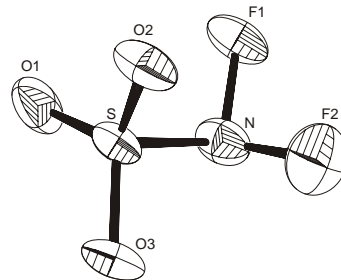
Colorless and air stable  $[\text{PNP}][\text{SO}_3\text{NF}_2]$  was obtained by neutralizing the fluorination reaction mixture, adding  $\text{PNP}^+\text{Cl}^-$  and extracting with methylene chloride [Eq (3)]. Single crystals of  $[\text{PNP}][\text{SO}_3\text{NF}_2]\cdot\text{CH}_2\text{Cl}_2$  suitable for X-ray crystal structure determination were obtained by recrystallization from  $\text{CH}_2\text{Cl}_2$ .



**Figure 1.** IR and Raman spectra of solid  $\text{NaSO}_3\text{NF}_2$ . Bands marked with asterisks (\*) are due to an impurity of  $\text{NO}_3^-$ .



$[\text{PNP}][\text{SO}_3\text{NF}_2]\cdot\text{CH}_2\text{Cl}_2$ , containing one molecule of methylene chloride, crystallizes in the triclinic space group  $P\bar{1}$ . The X-ray structure analysis<sup>[15]</sup> reveals the presence of two isolated  $[\text{PNP}]^+$  and  $[\text{SO}_3\text{NF}_2]^-$  units together with two disordered  $\text{CH}_2\text{Cl}_2$  molecules in the unit cell (packing diagrams are given in the Supplementary Figures S1 and S2). The closest F...H and O...H contacts between neighboring cations and anions are 2.682  $\text{\AA}$  and 2.349  $\text{\AA}$ , respectively. The  $\text{SO}_3\text{NF}_2^-$  anion is depicted in Figure 2. The dimen-



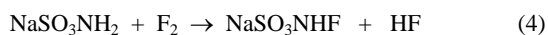
**Figure 2.** ORTEP drawing of the anion part of  $[\text{PNP}][\text{SO}_3\text{NF}_2]\cdot\text{CH}_2\text{Cl}_2$ . Thermal ellipsoids are shown at the 50% probability level. Bond lengths [ $\text{\AA}$ ] and angles [ $^\circ$ ]: S–O(1) 1.428(4), S–O(2) 1.424(3), S–O(3) 1.424(3), S–N 1.772(4), F(1)–N 1.412(5), F(2)–N 1.463(6), O(1)–S–O(2) 114.7(2), O(1)–S–O(3) 116.1(2), O(2)–S–O(3) 116.8(2), O(1)–S–N 100.1(2), O(2)–S–N 106.1(2), O(3)–S–N 99.3(2), F(1)–N–F(2) 99.0(3), F(1)–N–S 104.5(3), F(2)–N–S 99.6(3).

sions of the  $\text{SO}_3\text{N}$  skeleton are more similar to those of sulfamic acid<sup>[16]</sup> than to the ones reported for salts with the  $\text{SO}_3\text{NH}_2^-$  anion.<sup>[17]</sup> Estimations of the double-bond character of the S–N bond are frequently made by comparison of the observed lengths with that predicted from Pauling's covalent radii, 1.74  $\text{\AA}$ ,<sup>[18]</sup> or with the bond length in sulfamic acid, 1.772(1)  $\text{\AA}$ .<sup>[16b]</sup> In the solid state, the latter has the zwitterionic structure  $^+\text{NH}_3\text{--SO}_3^-$  which possesses a formal

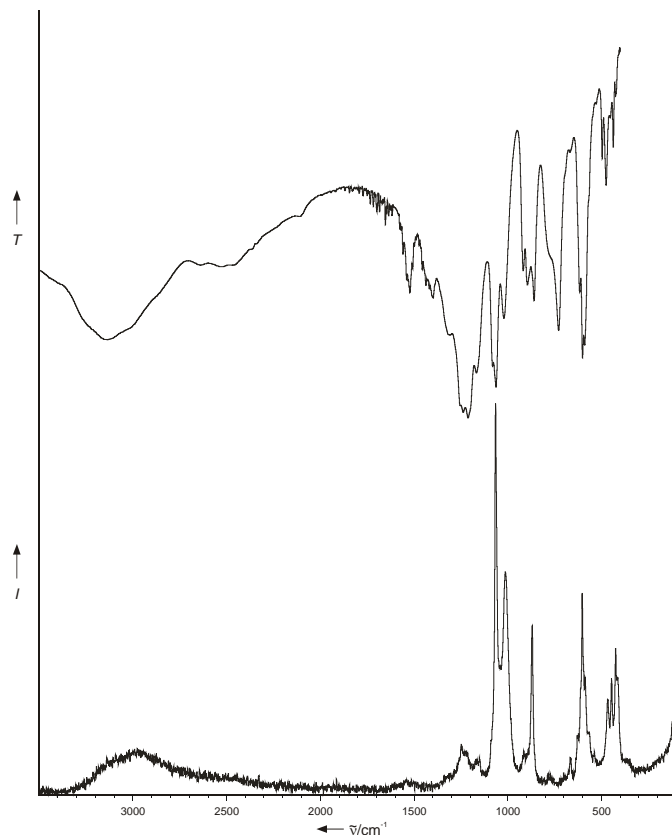
S–N single bond. The observed S–N bond length of 1.772(4) Å in  $\text{SO}_3\text{NF}_2^-$  is similar to the one in sulfamic acid and larger than the typical values found in the  $\text{SO}_3\text{NH}_2^-$  anion (1.64 Å). The S–O bond lengths of 1.428(8) Å and 1.424(3) Å are shorter than the values reported for sulfamates (1.44–1.45 Å)<sup>[17]</sup> and sulfamic acid (1.438(1) Å, 1.436(1) Å, and 1.435(1) Å).<sup>[16b]</sup> The average O–S–O and O–S–N angles of 115.9° and 101.8°, respectively, are in good agreement with the ones reported for sulfamic acid.

The marked differences in the S–N and S–O bond lengths between  $\text{SO}_3\text{NF}_2^-$  and  $\text{SO}_3\text{NH}_2^-$  can be readily reconciled by the large difference between the electronegativities of hydrogen and fluorine. The strongly electron withdrawing fluorine atoms pull some of the negative charges away from the oxygen atoms, thereby increasing the S=O double bond character and shortening the S–O bonds. By contrast, the electron-donating hydrogen atoms increase the electron density on the nitrogen atom, which passes it on to the S=O bonds. This results in partial N=S double bond character and increased negative charges on the oxygen atoms with concomitant lengthening of the S–O bonds.

When only one equivalent of fluorine was used in the fluorination reaction of  $\text{SO}_3\text{NH}_2^-$ , the  $\text{SO}_3\text{NHF}^-$  anion was formed [Eq. (4)].



Colorless and somewhat moisture sensitive  $\text{NaSO}_3\text{NHF}$  was obtained when the acidic reaction mixture was evaporated in a vacuum at 0 °C. The compound was identified and characterized by its vibrational spectra and, as  $[\text{PPh}_4][\text{SO}_3\text{NHF}]$ , by its crystal structure. The observed Raman and IR spectra of  $\text{NaSO}_3\text{NHF}$  are shown in Figure 3. The observed frequencies and intensities are listed in Table 2 and were assigned by comparison with those calculated at the MP2<sup>[11]</sup> level of theory using the 6-311+G(d) basis set.

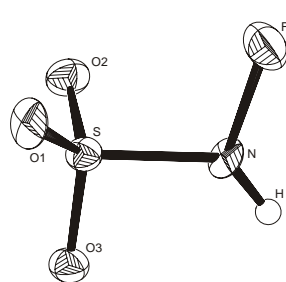


**Figure 3.** IR and Raman spectra of solid  $\text{NaSO}_3\text{NHF}$ .

**Table 2.** Comparison of observed and unscaled calculated MP2/6-311+G(d) vibrational frequencies ( $\text{cm}^{-1}$ ) and intensities for  $\text{SO}_3\text{NHF}^-$  in point group  $\text{C}_1$ .

mode	approx. mode description in point group $\text{C}_1$	observed <sup>[a],[d]</sup>		calculated <sup>[b]</sup>
		IR	Raman	calcd (IR) [Raman]
$\nu_1$	$\nu_s$ NHF	3100 s, br	3000 [1.3]	3481 (2.4) [69]
$\nu_2$	$\nu_{as}$ NHF	1522 w		1410 (30) [2.8]
$\nu_3$	$\nu_{as}$ $\text{SO}_3$	1242 vs	1246 [1.3]	1270 (368) [7.3]
$\nu_4$	$\nu_{as}$ $\text{SO}_3$	1213 vs	1225 [1.2]	1240 (401) [7.1]
$\nu_5$	$\nu_s$ $\text{SO}_3$	1064 s	1065 [10.0]	1041 (82) [27]
$\nu_6$	$\delta$ NHF	1021 m	1014 [5.9]	1033 (45) [18]
$\nu_7$	$\delta$ NHF	863 m	869 [4.3]	923 (38) [14]
$\nu_8$	$\nu$ SN	602 s	602 [5.0]	699 (161) [16]
$\nu_9$	$\delta_{sciss}$ $\text{SO}_2$	590 s		584 (66) [4.5]
$\nu_{10}$	$\delta_{sciss}$ $\text{SO}_2$	497 w	466 [2.6]	520 (26) [3.4]
$\nu_{11}$	$\delta_{umbrella}$ $\text{SO}_2$	477 w	445 [3.0]	509 (26) [5.9]
$\nu_{12}$	$\delta_{rock}$ $\text{SO}_2$	438 w	424 [3.7]	371 (0.1) [4.7]
$\nu_{13}$	$\delta_{rock}$ $\text{SO}_2$	[c]	411 [3.0]	343 (8.1) [2.6]
$\nu_{14}$	$\delta$ NHF	[c]		215 (1.2) [1.1]
$\nu_{15}$	$\tau$ SN	[c]	122 [2.0]	118 (1.9) [0.4]

[a] As  $\text{Na}^+$  salt. Relative IR and Raman intensities given in parentheses and brackets, respectively. [b] IR intensities given in  $\text{km mol}^{-1}$  and Raman intensities given in  $\text{\AA}^4 \text{amu}^{-1}$ . [c] Not observed, IR spectrum recorded only between 4000 and 400  $\text{cm}^{-1}$ . [d] In addition to the listed bands, IR bands at 1313 m, 1168 s, 1082 s, 918 m, 897 m, 773 m, 731 s, 617 m and Raman bands at 1168 [1.0], 1153 [1.0], 913 [1.2], 666 [1.0]  $\text{cm}^{-1}$  were observed which were not assigned.



**Figure 4.** ORTEP drawing of the anion part of  $[\text{PPh}_4][\text{SO}_3\text{NHF}]$ . Thermal ellipsoids are shown at the 50% probability level. Selected bond lengths [Å] and angles [°]: S–O(1) 1.433(4), S–O(2) 1.457(4), S–O(3) 1.447(3), S–N 1.694(5), F(1)–N 1.474(5), O(1)–S–O(2) 114.4(2), O(1)–S–O(3) 115.3(2), O(2)–S–O(3) 114.1(2), O(1)–S–N 108.5(2), O(2)–S–N 104.3(2), O(3)–S–N 98.0(2), F–N–S 106.4(3).

The  $[\text{PPh}_4][\text{SO}_3\text{NHF}]$  salt was obtained by metathesis in the same manner as shown in Eq. 3. It crystallizes disordered in the triclinic space group  $P\bar{1}$ . The X-ray structure analysis<sup>[19]</sup> reveals the presence of two non-equivalent  $[\text{PPh}_4]^+$  and  $[\text{SO}_3\text{NHF}]^-$  units (packing diagrams are given in the Supplementary Figures S3 and S4). While one  $\text{SO}_3\text{NHF}^-$  anion could be refined well, the second one suffers from a disorder in the  $\text{SO}_3$ -group. This results in a relatively high R factor of 8.16% for the refined structure. The closest F...H and O...H contacts between neighboring cations and anions are 2.566 Å and 2.373 Å, respectively. The ordered  $\text{SO}_3\text{NHF}^-$  anion is depicted in Figure 4. The observed S–N bond

length of 1.694(5) Å in  $\text{SO}_3\text{NHF}^-$  lies between those observed for  $\text{SO}_3\text{NF}_2^-$  (1.772(4) Å) and  $\text{SO}_3\text{NH}_2^-$  (1.64 Å). This is in accord with the expectation that the electronic effect of an  $-\text{NHF}$  group is intermediate between those of an  $-\text{NF}_2$  and an  $-\text{NH}_2$  group.

The presence of one hydrogen atom and one fluorine atom attached to the same nitrogen atom was further established by proton and fluorine NMR spectroscopy. The proton and fluorine spectra showed doublets at  $\delta = 8.69$  and  $-103.0$  ppm, respectively, with the same  $^2J(^1\text{H}-^{19}\text{F})$  coupling constant of 49 Hz.

The utility of  $\text{NaSO}_3\text{NF}_2$  as an alternative source of difluoramine in organic difluoramination reactions was demonstrated by both research groups. At TPL, qualitative reactions of cyclohexanone and of 3-pentanone with the reagent in  $\sim 100\%$   $\text{H}_2\text{SO}_4$  showed in both cases formation of the expected *gem*-bis(difluoramino)alkane by  $^{19}\text{F}$  NMR spectroscopy. A quantitative comparison was conducted using 1,3-dibromoacetone as a model ketone. Using  $\text{NaSO}_3\text{NF}_2$  in anhydrous  $\text{H}_2\text{SO}_4$  containing  $\sim 1\%$   $\text{SO}_3$ , 1,3-dibromo-2,2-bis(difluoramino)propane was formed in 38% nonoptimized yield. This compares with a yield of 37% for conventional difluoramination ( $\text{HNF}_2$  in oleum) of 1,3-dibromoacetone.

At USC, the potential of  $\text{NaSO}_3\text{NF}_2$  for the transformation of carbonyl into *gem*-bis(difluoramino) groups was demonstrated for acetone and 1-acetylpiperidin-4-one using 2.5 equivalents of the reagent in  $\text{CDCl}_3$  containing 30% oleum. The formation of the desired *gem*-bis(difluoramino) compounds was established by  $^{19}\text{F}$ ,  $^1\text{H}$ , and  $^{13}\text{C}$  NMR spectroscopy. In the case of 1-acetylpiperidin-4-one, only the oxygen of the ring-carbonyl group was replaced, while the carbonyl oxygen of the acetyl group did not react.

In summary, the elusive difluorosulfamate and monofluorosulfamate anions have been isolated and characterized for the first time. They can be prepared in high yield by direct fluorination of sulfamates in aqueous solution. The absence of prior reports of isolation of these salts may be attributed to rapid acid-catalyzed hydrolysis of these solutions above 0 °C. The  $\text{NaSO}_3\text{NF}_2$  salt is a stable, storable reagent for the *in-situ* generation of  $\text{HNF}_2$  and preparation of *gem*-bis(difluoramino) compounds, eliminating the hazards involved in the isolation and handling of treacherous difluoramine.

## Experimental Section

**Sodium difluorosulfamate (TPL):** Sulfamic acid (16.42 g, 0.169 mol) was dissolved in 30 mL  $\text{H}_2\text{O}$ , and  $\text{NaOH}$  (8.1 g, 0.20 mol), was added. Fluorine (10% in nitrogen) was bubbled through the solution at 0 °C. The progress of the fluorination of sulfamate was monitored by  $^{19}\text{F}$  NMR analysis of reaction aliquots, observing the conversion of monofluorosulfamate ( $\delta = -102.1$  ppm vs. external  $\text{CFCl}_3$  in  $[\text{D}_6]\text{acetone}$ ) to difluorosulfamate ( $\delta = 36.6$  ppm). After 1.5 h, the fluorination was complete, and the cloudy mixture was neutralized with concentrated aqueous  $\text{NaOH}$ . The  $\text{NaF}$  precipitate was removed by filtration. Based on its  $^{19}\text{F}$  NMR spectrum, the filtrate appeared to be a 96 : 4 mixture of  $\text{NaSO}_3\text{NF}_2$  and  $\text{NaF}$ . The viscous filtrate was quickly dried at room temperature in a vacuum desiccator over excess  $\text{P}_2\text{O}_5$ . After 24 h,  $^{19}\text{F}$  NMR analysis of the dried solid showed the same  $\text{SO}_3\text{NF}_2^-/\text{F}^-$  ratio as the initial filtrate.

**1,3-Dibromo-2,2-bis(difluoramino)propane (TPL):** 1,3-Dibromoacetone (24.72 g, 0.114 mol) was added to a mixture of sodium difluorosulfamate (61 g,  $\leq 0.39$  mol) in 310 mL of sulfuric acid containing  $\sim 1\%$   $\text{SO}_3$  (made from 30% oleum plus conc.  $\text{H}_2\text{SO}_4$ ) plus 100 mL dichloromethane. After stirring for 4 days at 0 °C, the reaction was quenched in water, neutralized, and extracted with dichloromethane. Removal of the solvent produced 13.2 g of solute, the major constituent of which was 1,3-dibromo-2,2-bis(difluoramino)propane (38% crude yield). Three short-path distillations (room temperature at 1–3 torr) produced material that was  $>95\%$  pure (elemental analysis

and  $^1\text{H}$  NMR) with residual 1,3-dibromoacetone as the main impurity.  $^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ , TMS):  $\delta$  3.98 (quintet, 1.25 Hz).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  23.75 (quintet, 5.5 Hz), 99 (m).  $^{19}\text{F}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  29.9 (s).  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  3.24 (quintet, 1.27 Hz).  $^{13}\text{C}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  23.69 (quintet, 5.7 Hz), 95.37 (quintet, 6.4 Hz).  $^{19}\text{F}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  30.26 (s). Anal. Calcd. for  $(0.953)\text{C}_3\text{H}_4\text{F}_4\text{N}_2\text{Br}_2 + (0.047)\text{C}_3\text{H}_4\text{Br}_2\text{O}$ : C, 12.08; H, 1.35; N, 8.78; F, 23.83. Found: C, 12.12; H, 1.30; N, 8.93; F, 23.53.

**Materials and Apparatus (USC):** All reactions were carried out in Teflon-FEP ampules closed by stainless steel valves or Pyrex glass vessels closed by grease-free Kontes glass-Teflon valves. Volatile materials were handled in stainless steel/Teflon-FEP<sup>[20]</sup> or Pyrex glass vacuum lines. Nonvolatile solids were handled in the dry argon atmosphere of a glove box. Infrared spectra were recorded in the range 4000–400  $\text{cm}^{-1}$  on a Midac, M Series, FT-IR spectrometer using KBr pellets. The pellets were prepared inside the glove box using an Econo mini-press (Barnes Engineering Co.) and transferred in a closed container to the spectrometer before placing them quickly into the sample compartment which was purged with dry nitrogen to minimize exposure to atmospheric moisture and potential hydrolysis of the sample. Raman spectra were recorded on a Bruker Equinox 55 FT-RA spectrometer using a Nd-YAG laser at 1064 nm with power levels of 100–200 mW and Pyrex melting point capillaries as sample containers.

Nuclear magnetic resonance spectra were recorded unlocked on Bruker AMX 500 and Varian Mercury/VX 400 NMR spectrometers at room temperature. The  $^{19}\text{F}$  and  $^{15}\text{N}$  NMR spectra were referenced to external samples of neat  $\text{CFCl}_3$  and neat nitromethane, respectively.

The starting materials  $\text{H}_2\text{NSO}_3\text{H}$ ,  $\text{H}_2\text{SO}_4$ ,  $[\text{P}(\text{C}_6\text{H}_5)_4]\text{Cl}$ ,  $[\text{PNP}]\text{Cl}$ ,  $\text{NaOH}$  (all Aldrich),  $^{15}\text{N}_2$ urea (MSD Isotopes), and fluorine (Air Products and Chemicals Inc.) were used without further purification. Solvents were dried by standard methods and freshly distilled prior to use.  $\text{NaSO}_3\text{NH}_2$  was obtained by neutralization of  $\text{HSO}_3\text{NH}_2$  with  $\text{NaOH}$ .  $^{15}\text{N}[\text{HSO}_3\text{NH}_2]$  was prepared from  $^{15}\text{N}_2$ urea and  $\text{H}_2\text{SO}_4$  according to a modified literature method.<sup>[21]</sup>

**Preparation of  $\text{NaSO}_3\text{NHF}$  (USC):** A solution of  $\text{NaSO}_3\text{NH}_2$  (0.380 g, 3.19 mmol) in 4 mL water was placed into a Teflon-FEP ampule equipped with a Teflon-coated magnetic stirring bar and a Teflon gas inlet tube. After cooling to 0 °C, fluorine (3.19 mmol), diluted by 90 vol.% nitrogen, was introduced at a rate of 110 mL/min. The reaction mixture was pumped to dryness at 0 °C, leaving behind a colorless solid (0.391 g, weight calculated for 3.19 mmol  $\text{NaSO}_3\text{NHF} = 0.437$  g).

**Preparation of  $[\text{PPh}_4][\text{SO}_3\text{NHF}]$  (USC):** A solution of  $\text{NaSO}_3\text{NH}_2$  (0.695 g, 5.00 mmol) in 10 mL water was placed into a Teflon-FEP ampule equipped with a magnetic stirring bar and a Teflon gas inlet tube. After cooling to 0 °C, fluorine (5.00 mmol), diluted by 90 vol.% nitrogen, was introduced at a rate of 110 mL/min. The reaction mixture was neutralized by adding cold solid  $\text{NaHCO}_3$  and filtered through a cold porcelain frit. A cold solution of 5.00 mmol  $\text{PPh}_4\text{Cl}$  in 50 mL water was added to the clear filtrate. The resulting milky solution was extracted three times with 50 mL of cold  $\text{CH}_2\text{Cl}_2$ . The combined organic phases were dried over  $\text{MgSO}_4$  and pumped to dryness at ambient temperature, leaving behind a colorless solid (2.039 g, weight calculated for 5.00 mmol  $\text{PPh}_4\text{SO}_3\text{NHF} = 2.267$  g). Crystals were grown from  $\text{CH}_2\text{Cl}_2$  solution by slow evaporation of the solvent using a stream of dry nitrogen.

**Preparation of  $\text{NaSO}_3\text{NF}_2$  (USC):** A solution of  $\text{NaSO}_3\text{NH}_2$  (0.236 g, 1.98 mmol) in 7 mL water was placed into a Teflon-FEP ampule equipped with a magnetic stirrer and a Teflon gas inlet tube. After cooling to 0 °C, fluorine, diluted by 90 vol.% nitrogen, was introduced at a rate of 110 mL/min. After 45 min, the fluorination was discontinued, and the reaction mixture pumped to dryness at 0 °C, leaving behind a colorless solid (0.288 g, weight calculated for 1.98 mmol  $\text{NaSO}_3\text{NF}_2 = 0.307$  g).

**Preparation of  $[\text{A}][\text{SO}_3\text{NF}_2]$  ( $\text{A} = \text{PNP}$ ,  $\text{PPh}_4$ ,  $\text{AsPh}_4$ ) (USC):** A solution of  $\text{NaSO}_3\text{NH}_2$  (0.357 g, 3.00 mmol) in 10 mL water was placed into a Teflon-FEP ampule equipped with a magnetic stirring bar and a Teflon gas inlet tube. After cooling to 0 °C, fluorine, diluted by 90 vol.% nitrogen, was introduced at a rate of 110 mL/min. After 60 min, the fluorination was discontinued, and the reaction mixture was

neutralized by adding cold solid  $\text{NaHCO}_3$ . The reaction mixture was filtered through a cold porcelain frit, and a cold aqueous solution of 3.00 mmol  $\text{A}^+\text{Cl}^-$  was added to the clear filtrate. The resulting milky solution was extracted three times with 10 mL of cold  $\text{CH}_2\text{Cl}_2$ . The combined organic phases were dried over  $\text{MgSO}_4$  and pumped to dryness at ambient temperature, leaving behind colorless solids ( $[\text{PPh}_4][\text{SO}_3\text{NF}_2]$ : 1.283 g, calculated weight for 3.00 mmol = 1.414 g;  $[\text{AsPh}_4][\text{SO}_3\text{NF}_2]$ : 1.466 g, calculated weight for 3.00 mmol = 1.543 g;  $[\text{PNP}][\text{SO}_3\text{NF}_2]$ : 2.071 g, calculated weight for 3.00 mmol = 2.011 g). Crystals were grown from  $\text{CH}_2\text{Cl}_2$  solution by slow evaporation of the solvent using a stream of dry nitrogen.

**2,2-Bis(difluoramino)propane and 1-acetyl-4,4-bis(difluoramino)piperidine (USC):** To a vigorously stirred mixture of  $\text{CDCl}_3$  (1.5 mL), 30% oleum (1.5 mL), and the ketone starting material (1.0 mmol), 2.5 equivalents of  $\text{NaSO}_3\text{NF}_2$  were added in increments at 4 °C. Immediate gas evolution was observed. After 15 min, the upper organic phase was analyzed by  $^{19}\text{F}$ ,  $^1\text{H}$ , and  $^{13}\text{C}$  NMR spectroscopy, showing the formation of the desired *gem*-bis(difluoramines).

**Theoretical Methods:** The molecular structures and harmonic vibrational frequencies were calculated using second-order many-body perturbation theory<sup>[14]</sup> (denoted as MP2, but also known as MBPT(2)) and a 6-311+G(d) basis set. Hessians (energy second derivatives) were calculated for the final equilibrium structures to determine if they are minima (positive definite hessian) or *n*th-order transition states ("*n*" negative eigenvalues). All calculations were performed using the electronic structure code GAMESS.<sup>[22]</sup>

Received: ((will be filled in by the editorial staff))

Published online on ((will be filled in by the editorial staff))

**Keywords:** *N,N*-difluorosulfamate · *N*-fluorosulfamate · fluorinated substituents · crystal struct. determination · *gem*-bis(difluoramino) compounds

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1223-336-033; e-mail: deposit@ccdc.cam.ac.uk) on quoting the deposition no. CCDC 274109.

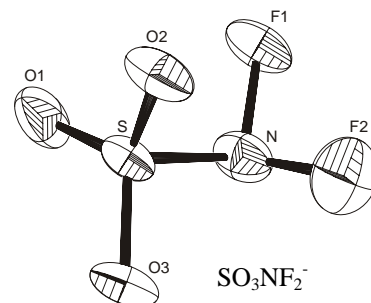
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*Synopsis*

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Preparation, Characterization, and  
Crystal Structures of the  $\text{SO}_3\text{NHF}^-$   
and  $\text{SO}_3\text{NF}_2^-$  Anions

**Safe difluoroaminating reagents:** Salts of the elusive  $\text{SO}_3\text{NF}_2^-$  anion were prepared by aqueous fluorination of  $\text{SO}_3\text{NH}_2^-$  with  $\text{F}_2$ , characterized, and shown to be excellent reagents for the preparation of *gem*-bis(difluoramines). Salts of the intermediate  $\text{SO}_3\text{NHF}^-$  anion were also isolated and characterized.





## Supplementary Material

Preparation, Characterization, and Crystal Structures of the  $\text{SO}_3\text{NH}^-$  and  $\text{SO}_3\text{NF}_2^-$  Anions

*Ralf Haiges,\* Ross Wagner, Jerry A. Boatz, Muhammed Yousufuddin, Markus Etzkorn, G. K. Surya Prakash, Karl O. Christe,\* Robert D. Chapman,\* Mark F. Welker, Charles B. Kreutzberger*

**Figure S1.** Crystal packing of  $[\text{PNP}][\text{SO}_3\text{NF}_2]\cdot\text{CH}_2\text{Cl}_2$  along the a-axis.

**Figure S2.** Crystal packing of  $[\text{PNP}][\text{SO}_3\text{NF}_2]\cdot\text{CH}_2\text{Cl}_2$  along the b\*-axis.

**Table S1.** Crystal data and structure refinement for  $[\text{PNP}][\text{SO}_3\text{NF}_2]\cdot\text{CH}_2\text{Cl}_2$ .

**Table S2.** Atomic coordinates and equivalent isotropic displacement parameters for  $[\text{PNP}][\text{SO}_3\text{NF}_2]\cdot\text{CH}_2\text{Cl}_2$ .

**Table S3.** Bond lengths and angles for  $[\text{PNP}][\text{SO}_3\text{NF}_2]\cdot\text{CH}_2\text{Cl}_2$ .

**Table S4.** Anisotropic displacement parameters for  $[\text{PNP}][\text{SO}_3\text{NF}_2]\cdot\text{CH}_2\text{Cl}_2$ .

**Figure S3.** Crystal packing of  $[\text{PPh}_4][\text{SO}_3\text{NFH}]$  along the a-axis.

**Figure S4.** Crystal packing of  $[\text{PPh}_4][\text{SO}_3\text{NFH}]$  along the b\*-axis.

**Table S5.** Crystal data and structure refinement for  $[\text{PPh}_4][\text{SO}_3\text{NFH}]$ .

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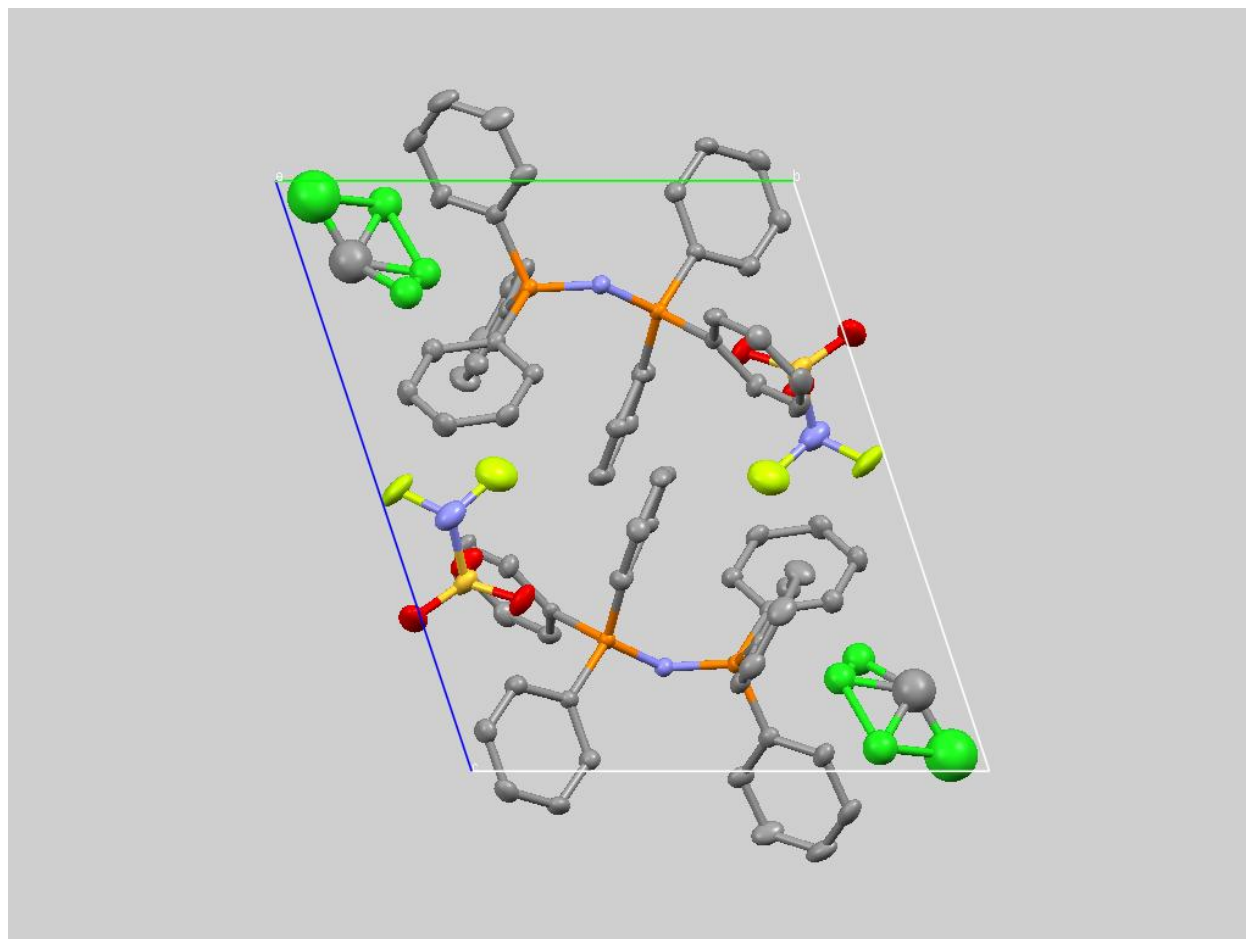
[\*\*] The work at USC was funded by the Air Force Office of Scientific Research, the Office of Naval Research, the Lawrence Livermore National Laboratory, and the National Science Foundation, and that at NAWCWD and TPL, Inc. was supported by the Office of Naval Research.

**Table S6.** Atomic coordinates and equivalent isotropic displacement parameters for [PPh<sub>4</sub>][SO<sub>3</sub>NFH].

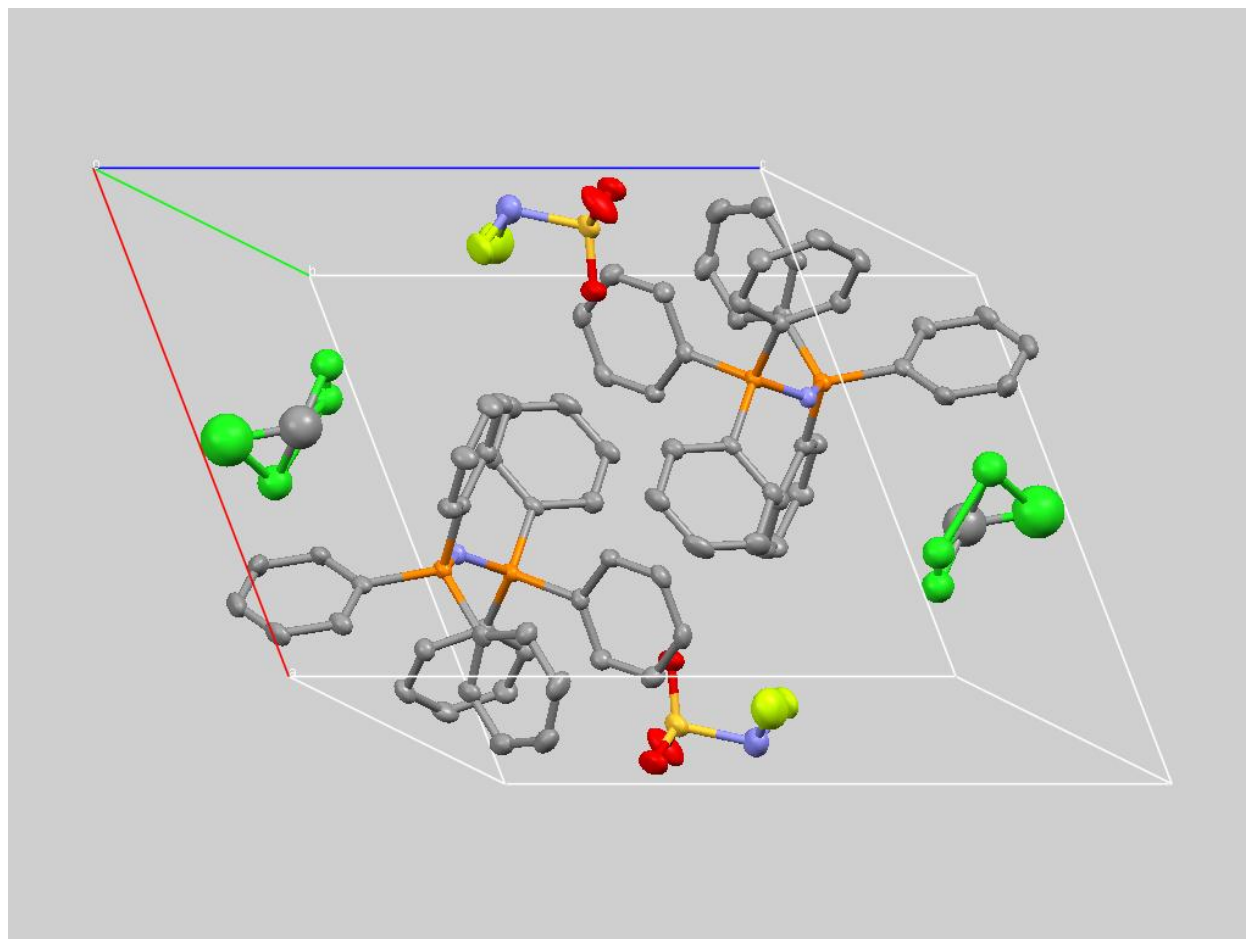
**Table S7.** Bond lengths and angles for [PPh<sub>4</sub>][SO<sub>3</sub>NFH].

**Table S8.** Anisotropic displacement parameters for [PPh<sub>4</sub>][SO<sub>3</sub>NFH]

**Figure S1.** Crystal packing of [PNP][SO<sub>3</sub>NF<sub>2</sub>] $\cdot$ CH<sub>2</sub>Cl<sub>2</sub> along the a-axis.



**Figure S2.** Crystal packing of [PNP][SO<sub>3</sub>NF<sub>2</sub>] $\cdot$ CH<sub>2</sub>Cl<sub>2</sub> along the b\*-axis.



**Table S1.** Crystal data and structure refinement for [PNP][SO<sub>3</sub>NF<sub>2</sub>] $\cdot$ CH<sub>2</sub>Cl<sub>2</sub>.

Identification code	pnpnf2m	
Empirical formula	C <sub>37</sub> H <sub>32</sub> Cl <sub>2</sub> F <sub>2</sub> N <sub>2</sub> O <sub>3</sub> P <sub>2</sub> S	
Formula weight	755.55	
Temperature	133(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 11.8650(12) Å	$\alpha = 66.755(2)^\circ$
	b = 11.9167(12) Å	$\beta = 68.964(2)^\circ$
	c = 14.5180(15) Å	$\gamma = 71.034(2)^\circ$
Volume	1719.7(3) Å <sup>3</sup>	
Z	2	
Density (calculated)	1.459 Mg/m <sup>3</sup>	
Absorption coefficient	0.395 mm <sup>-1</sup>	
F(000)	780	
Crystal size	0.29 x 0.21 x 0.05 mm <sup>3</sup>	
Theta range for data collection	1.58 to 27.49°	
Index ranges	-15 ≤ h ≤ 12, -15 ≤ k ≤ 12, -18 ≤ l ≤ 18	
Reflections collected	10657	
Independent reflections	7433 [R(int) = 0.0487]	
Completeness to theta = 27.49°	94.0 %	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F <sup>2</sup>	
Data / restraints / parameters	7433 / 0 / 439	
Goodness-of-fit on F <sup>2</sup>	1.012	
Final R indices [I > 2σ(I)]	R1 = 0.0731, wR2 = 0.1949	
R indices (all data)	R1 = 0.1087, wR2 = 0.2102	
Largest diff. peak and hole	2.141 and -0.956 e.Å <sup>-3</sup>	

**Table S2.** Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for [PNP][SO<sub>3</sub>NF<sub>2</sub>] $\cdot$ CH<sub>2</sub>Cl<sub>2</sub>. U(eq) is defined as one third of the trace of the orthogonalized U<sup>ij</sup> tensor.

	x	y	z	U(eq)
S(1)	9080(1)	8911(1)	3198(1)	33(1)
P(1)	6575(1)	6553(1)	2214(1)	18(1)
P(2)	7010(1)	4204(1)	1823(1)	19(1)
F(1)	8484(3)	9637(3)	4760(2)	54(1)
F(2)	9027(3)	7620(4)	5028(3)	82(1)
O(1)	9241(4)	10151(3)	2582(3)	61(1)
O(2)	7839(3)	8757(3)	3531(3)	42(1)
O(3)	10023(3)	7924(3)	2894(3)	41(1)
N(1)	6408(3)	5618(3)	1759(2)	20(1)
N(2)	9444(4)	8771(4)	4326(3)	47(1)
Cl(1)	5775(2)	1958(3)	400(2)	63(1)
Cl(2)	3499(3)	1805(3)	1898(2)	54(1)
Cl(3)	5216(5)	638(5)	269(5)	144(3)
Cl(4)	4060(5)	2288(5)	1569(4)	53(2)
C(1)	7440(3)	7663(4)	1214(3)	19(1)
C(2)	7860(4)	7649(4)	191(3)	25(1)
C(3)	8489(4)	8545(4)	-583(3)	28(1)
C(4)	8704(4)	9453(4)	-336(3)	30(1)
C(5)	8293(4)	9474(4)	677(3)	30(1)
C(6)	7658(4)	8594(4)	1450(3)	26(1)
C(7)	5076(3)	7436(3)	2706(3)	19(1)
C(8)	4889(4)	7971(4)	3466(3)	26(1)
C(9)	3748(4)	8680(4)	3804(4)	32(1)
C(10)	2791(4)	8856(4)	3404(4)	37(1)
C(11)	2955(4)	8324(4)	2660(4)	33(1)
C(12)	4093(4)	7619(4)	2315(3)	26(1)
C(13)	7258(4)	5804(4)	3290(3)	20(1)
C(14)	6615(4)	5020(4)	4190(3)	23(1)
C(15)	7116(4)	4356(4)	5015(3)	27(1)
C(16)	8267(4)	4462(4)	4968(3)	27(1)
C(17)	8906(4)	5239(4)	4085(3)	29(1)

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C(18)	8419(4)	5903(4)	3237(3)	25(1)
C(19)	5957(3)	3219(4)	2723(3)	20(1)
C(20)	6282(4)	1943(4)	2877(3)	27(1)
C(21)	5452(4)	1195(4)	3588(4)	31(1)
C(22)	4326(4)	1700(4)	4135(4)	32(1)
C(23)	3999(4)	2970(4)	3979(3)	29(1)
C(24)	4806(4)	3728(4)	3278(3)	24(1)
C(25)	7338(4)	4042(4)	568(3)	22(1)
C(26)	6609(4)	4827(4)	-94(3)	29(1)
C(27)	6838(4)	4679(5)	-1051(4)	37(1)
C(28)	7804(4)	3750(5)	-1349(4)	38(1)
C(29)	8536(4)	2972(4)	-700(4)	35(1)
C(30)	8311(4)	3098(4)	269(3)	28(1)
C(31)	8442(4)	3632(4)	2177(3)	21(1)
C(32)	8589(4)	2708(4)	3100(3)	29(1)
C(33)	9685(5)	2384(5)	3362(4)	40(1)
C(34)	10632(4)	2982(5)	2710(4)	40(1)
C(35)	10507(4)	3908(4)	1780(4)	34(1)
C(36)	9415(4)	4230(4)	1512(3)	27(1)
C(37)	4897(7)	940(8)	1366(7)	98(3)

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**Table S3.** Bond lengths [ $\text{\AA}$ ] and angles [ $^\circ$ ] for  $[\text{PNP}][\text{SO}_3\text{NF}_2]\cdot\text{CH}_2\text{Cl}_2$ .

Cl(1)-C(37)	1.718(9)	C(15)-C(16)	1.387(6)
Cl(2)-C(37)	1.735(9)	C(16)-C(17)	1.377(6)
Cl(3)-C(37)	1.656(10)	C(17)-C(18)	1.386(6)
Cl(3)-Cl(3)#1	2.216(11)	C(19)-C(20)	1.387(5)
Cl(4)-C(37)	1.667(9)	C(19)-C(24)	1.393(5)
S(1)-O(2)	1.424(3)	C(20)-C(21)	1.394(6)
S(1)-O(3)	1.424(3)	C(21)-C(22)	1.368(6)
S(1)-O(1)	1.428(4)	C(22)-C(23)	1.379(6)
S(1)-N(2)	1.772(4)	C(23)-C(24)	1.381(6)
P(1)-N(1)	1.593(3)	C(25)-C(26)	1.382(6)
P(1)-C(1)	1.791(4)	C(25)-C(30)	1.403(5)
P(1)-C(13)	1.798(4)	C(26)-C(27)	1.388(6)
P(1)-C(7)	1.801(4)	C(27)-C(28)	1.387(6)
P(2)-N(1)	1.581(3)	C(28)-C(29)	1.370(7)
P(2)-C(31)	1.792(4)	C(29)-C(30)	1.393(6)
P(2)-C(19)	1.793(4)	C(31)-C(32)	1.384(6)
P(2)-C(25)	1.796(4)	C(31)-C(36)	1.403(6)
F(1)-N(2)	1.412(5)	C(32)-C(33)	1.378(6)
F(2)-N(2)	1.463(6)	C(33)-C(34)	1.375(7)
C(1)-C(2)	1.392(5)	C(34)-C(35)	1.387(7)
C(1)-C(6)	1.403(5)	C(35)-C(36)	1.378(6)
C(2)-C(3)	1.389(6)		
C(3)-C(4)	1.384(6)	C(37)-Cl(3)-Cl(3)#1	137.9(6)
C(4)-C(5)	1.382(6)	O(2)-S(1)-O(3)	116.78(19)
C(5)-C(6)	1.380(6)	O(2)-S(1)-O(1)	114.7(2)
C(7)-C(12)	1.394(5)	O(3)-S(1)-O(1)	116.1(2)
C(7)-C(8)	1.400(5)	O(2)-S(1)-N(2)	106.1(2)
C(8)-C(9)	1.377(6)	O(3)-S(1)-N(2)	99.3(2)
C(9)-C(10)	1.376(6)	O(1)-S(1)-N(2)	100.1(2)
C(10)-C(11)	1.383(6)	N(1)-P(1)-C(1)	111.00(18)
C(11)-C(12)	1.374(6)	N(1)-P(1)-C(13)	114.57(17)
C(13)-C(18)	1.393(5)	C(1)-P(1)-C(13)	109.73(18)
C(13)-C(14)	1.395(5)	N(1)-P(1)-C(7)	109.01(18)
C(14)-C(15)	1.367(6)	C(1)-P(1)-C(7)	106.65(18)

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C(13)-P(1)-C(7)	105.44(18)	C(16)-C(17)-C(18)	120.7(4)
N(1)-P(2)-C(31)	113.78(17)	C(17)-C(18)-C(13)	119.4(4)
N(1)-P(2)-C(19)	110.66(18)	C(20)-C(19)-C(24)	119.3(4)
C(31)-P(2)-C(19)	109.00(19)	C(20)-C(19)-P(2)	120.4(3)
N(1)-P(2)-C(25)	109.02(18)	C(24)-C(19)-P(2)	120.3(3)
C(31)-P(2)-C(25)	106.69(18)	C(19)-C(20)-C(21)	119.4(4)
C(19)-P(2)-C(25)	107.44(18)	C(22)-C(21)-C(20)	121.0(4)
P(2)-N(1)-P(1)	134.0(2)	C(21)-C(22)-C(23)	119.7(4)
F(1)-N(2)-F(2)	99.0(3)	C(22)-C(23)-C(24)	120.2(4)
F(1)-N(2)-S(1)	104.5(3)	C(23)-C(24)-C(19)	120.4(4)
F(2)-N(2)-S(1)	99.6(3)	C(26)-C(25)-C(30)	119.7(4)
C(2)-C(1)-C(6)	119.1(4)	C(26)-C(25)-P(2)	119.9(3)
C(2)-C(1)-P(1)	120.9(3)	C(30)-C(25)-P(2)	120.3(3)
C(6)-C(1)-P(1)	119.9(3)	C(25)-C(26)-C(27)	120.0(4)
C(3)-C(2)-C(1)	120.3(4)	C(26)-C(27)-C(28)	120.2(4)
C(4)-C(3)-C(2)	119.9(4)	C(29)-C(28)-C(27)	120.2(4)
C(5)-C(4)-C(3)	120.3(4)	C(28)-C(29)-C(30)	120.4(4)
C(6)-C(5)-C(4)	120.2(4)	C(29)-C(30)-C(25)	119.4(4)
C(5)-C(6)-C(1)	120.2(4)	C(32)-C(31)-C(36)	119.6(4)
C(12)-C(7)-C(8)	119.1(4)	C(32)-C(31)-P(2)	123.1(3)
C(12)-C(7)-P(1)	120.2(3)	C(36)-C(31)-P(2)	117.1(3)
C(8)-C(7)-P(1)	120.7(3)	C(33)-C(32)-C(31)	120.0(4)
C(9)-C(8)-C(7)	119.7(4)	C(32)-C(33)-C(34)	120.1(5)
C(10)-C(9)-C(8)	120.2(4)	C(33)-C(34)-C(35)	120.9(4)
C(9)-C(10)-C(11)	120.9(4)	C(36)-C(35)-C(34)	119.2(4)
C(12)-C(11)-C(10)	119.3(4)	C(35)-C(36)-C(31)	120.2(4)
C(11)-C(12)-C(7)	120.7(4)	Cl(3)-C(37)-Cl(4)	124.3(6)
C(18)-C(13)-C(14)	119.4(4)	Cl(3)-C(37)-Cl(1)	72.3(4)
C(18)-C(13)-P(1)	123.2(3)	Cl(4)-C(37)-Cl(1)	79.6(4)
C(14)-C(13)-P(1)	117.3(3)	Cl(3)-C(37)-Cl(2)	124.2(5)
C(15)-C(14)-C(13)	120.5(4)	Cl(4)-C(37)-Cl(2)	30.5(2)
C(14)-C(15)-C(16)	120.3(4)	Cl(1)-C(37)-Cl(2)	108.4(5)
C(17)-C(16)-C(15)	119.6(4)		

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Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y,-z

**Table S4.** Anisotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for [PNP][SO<sub>3</sub>NF<sub>2</sub>] $\cdot$ CH<sub>2</sub>Cl<sub>2</sub>. The anisotropic displacement factor exponent takes the form:  $-2\pi^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$ .

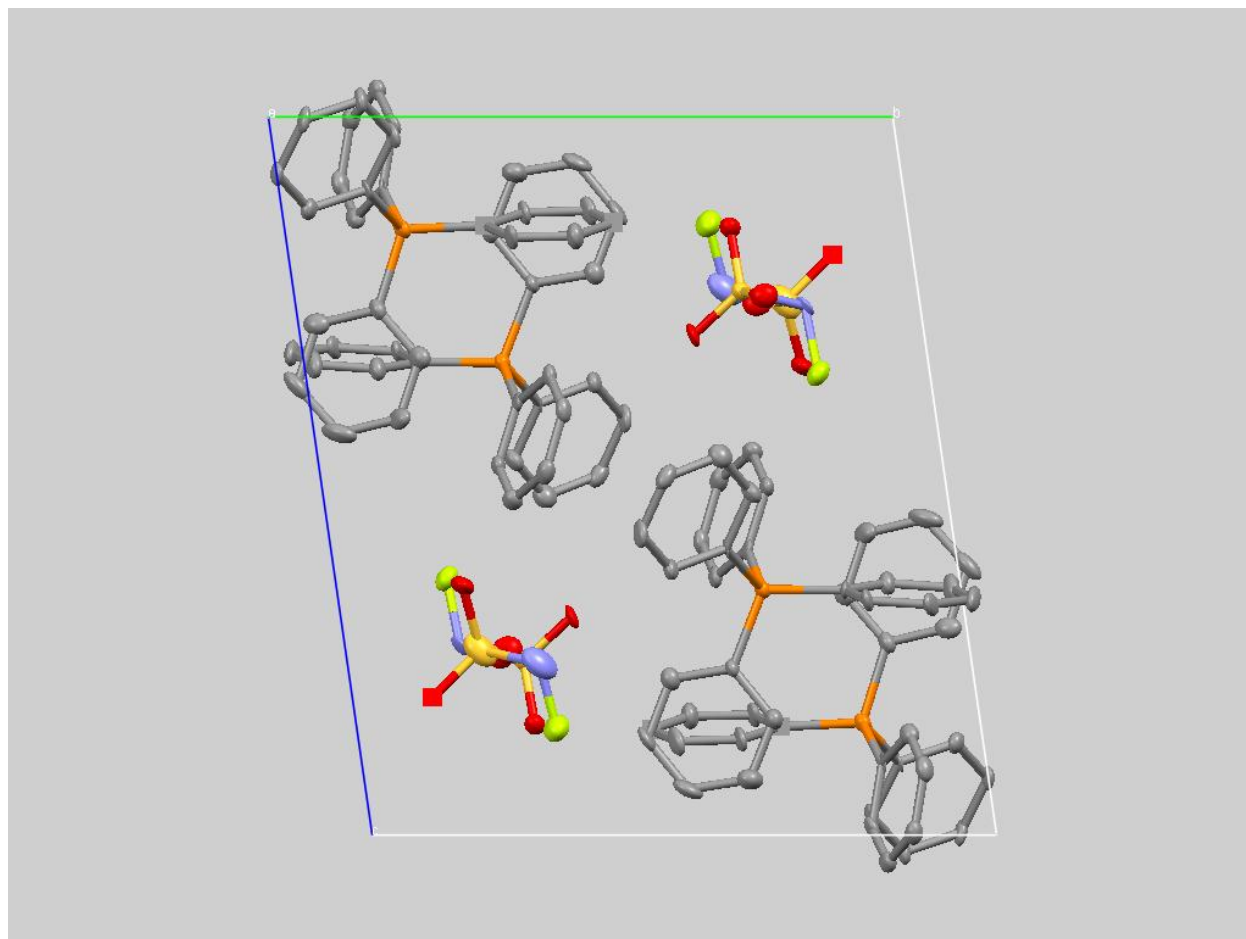
	U <sup>11</sup>	U <sup>22</sup>	U <sup>33</sup>	U <sup>23</sup>	U <sup>13</sup>	U <sup>12</sup>
S(1)	29(1)	40(1)	32(1)	-22(1)	1(1)	-8(1)
P(1)	19(1)	18(1)	16(1)	-6(1)	-1(1)	-5(1)
P(2)	20(1)	20(1)	18(1)	-9(1)	-1(1)	-6(1)
F(1)	51(2)	70(2)	52(2)	-48(2)	4(2)	-12(2)
F(2)	86(3)	84(3)	64(3)	-11(2)	-29(2)	-9(2)
O(1)	77(3)	39(2)	39(2)	-8(2)	16(2)	-17(2)
O(2)	25(2)	66(2)	44(2)	-34(2)	1(2)	-12(2)
O(3)	30(2)	48(2)	51(2)	-36(2)	3(2)	-6(2)
N(1)	22(2)	20(2)	19(2)	-8(2)	-5(1)	-4(1)
N(2)	42(3)	60(3)	46(3)	-31(3)	-10(2)	-6(2)
C(1)	19(2)	19(2)	17(2)	-5(2)	-2(2)	-4(2)
C(2)	28(2)	25(2)	23(2)	-9(2)	-5(2)	-7(2)
C(3)	32(2)	29(2)	17(2)	-6(2)	1(2)	-8(2)
C(4)	25(2)	27(2)	27(3)	-2(2)	0(2)	-10(2)
C(5)	33(2)	26(2)	31(3)	-8(2)	-5(2)	-13(2)
C(6)	30(2)	27(2)	22(2)	-9(2)	-3(2)	-9(2)
C(7)	20(2)	16(2)	16(2)	-4(2)	2(2)	-4(2)
C(8)	25(2)	25(2)	30(3)	-14(2)	-4(2)	-5(2)
C(9)	30(2)	33(3)	32(3)	-20(2)	5(2)	-9(2)
C(10)	26(2)	30(3)	39(3)	-13(2)	6(2)	0(2)
C(11)	25(2)	32(3)	35(3)	-7(2)	-8(2)	0(2)
C(12)	27(2)	28(2)	18(2)	-6(2)	-4(2)	-5(2)
C(13)	25(2)	19(2)	18(2)	-6(2)	-5(2)	-6(2)
C(14)	20(2)	27(2)	20(2)	-7(2)	-2(2)	-8(2)
C(15)	31(2)	26(2)	18(2)	-7(2)	0(2)	-8(2)
C(16)	33(2)	27(2)	22(2)	-9(2)	-12(2)	-1(2)
C(17)	26(2)	30(2)	33(3)	-10(2)	-10(2)	-6(2)
C(18)	26(2)	25(2)	23(2)	-6(2)	-4(2)	-9(2)
C(19)	19(2)	21(2)	22(2)	-9(2)	-4(2)	-5(2)
C(20)	25(2)	27(2)	29(2)	-10(2)	-3(2)	-8(2)
C(21)	31(2)	22(2)	36(3)	-9(2)	-3(2)	-9(2)

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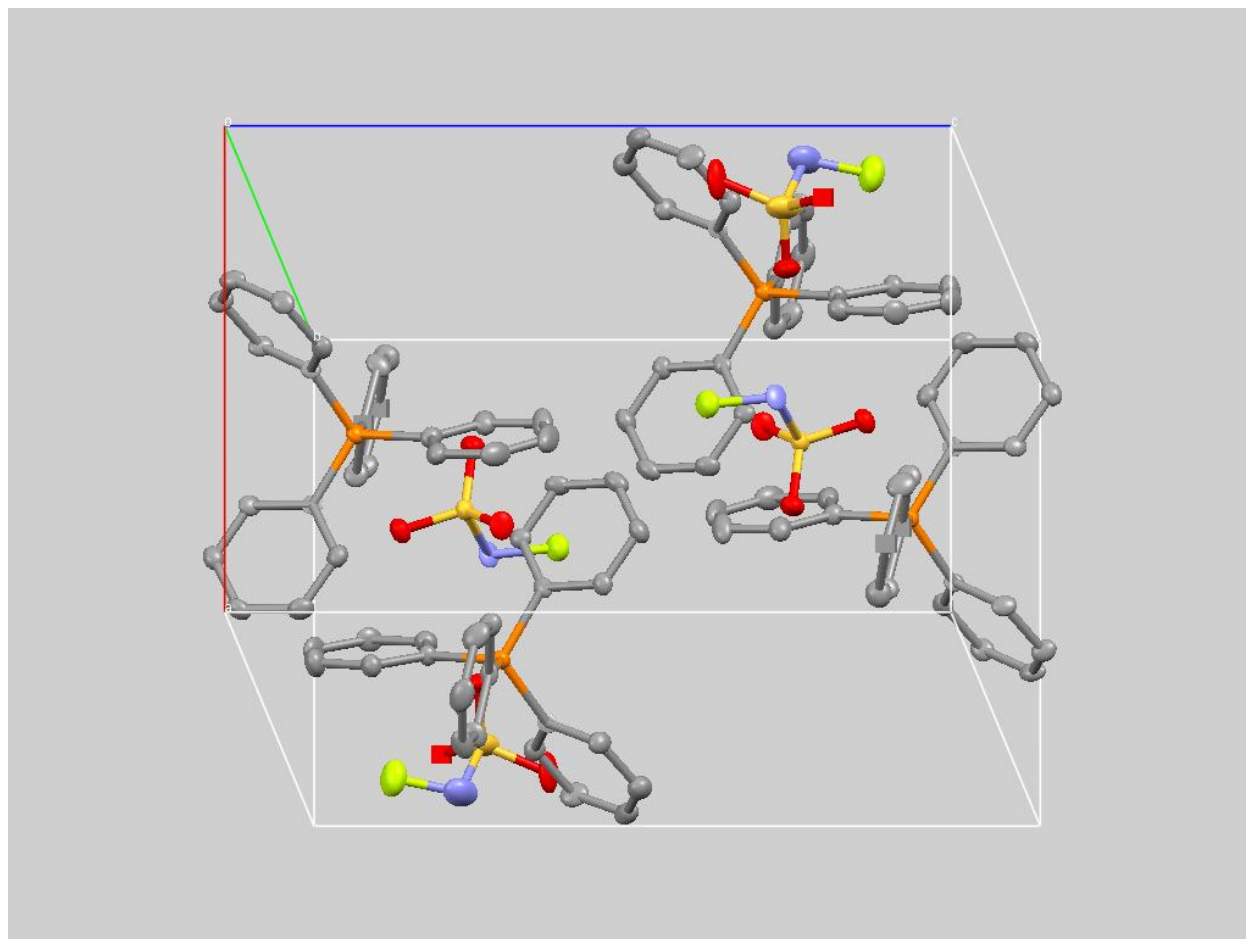
C(22)	34(3)	30(3)	30(3)	-7(2)	0(2)	-17(2)
C(23)	23(2)	34(3)	27(2)	-16(2)	2(2)	-6(2)
C(24)	25(2)	25(2)	23(2)	-9(2)	-4(2)	-7(2)
C(25)	20(2)	25(2)	22(2)	-10(2)	0(2)	-10(2)
C(26)	19(2)	42(3)	25(2)	-16(2)	0(2)	-6(2)
C(27)	27(2)	60(3)	31(3)	-20(3)	-10(2)	-9(2)
C(28)	38(3)	60(3)	27(3)	-25(3)	2(2)	-22(3)
C(29)	31(3)	39(3)	35(3)	-25(2)	6(2)	-10(2)
C(30)	28(2)	28(2)	30(3)	-16(2)	1(2)	-9(2)
C(31)	23(2)	18(2)	22(2)	-12(2)	-3(2)	-1(2)
C(32)	30(2)	31(3)	28(2)	-8(2)	-10(2)	-9(2)
C(33)	47(3)	44(3)	35(3)	-3(2)	-24(2)	-13(2)
C(34)	31(3)	54(3)	46(3)	-26(3)	-16(2)	-4(2)
C(35)	26(2)	44(3)	38(3)	-23(2)	-3(2)	-9(2)
C(36)	25(2)	29(2)	28(2)	-16(2)	1(2)	-6(2)

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**Figure S3.** Crystal packing of [PPh<sub>4</sub>][SO<sub>3</sub>NFH] along the a-axis.



**Figure S4.** Crystal packing of [PPh<sub>4</sub>][SO<sub>3</sub>NFH] along the b\*-axis.



**Table S5.** Crystal data and structure refinement for [PPh<sub>4</sub>][SO<sub>3</sub>NFH].

Identification code	nf23m	
Empirical formula	C <sub>24</sub> H <sub>21</sub> FNO <sub>3</sub> PS	
Formula weight	453.45	
Temperature	153(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 10.3914(18) Å	$\alpha = 82.221(3)^\circ$
	b = 14.094(2) Å	$\beta = 89.994(3)^\circ$
	c = 15.505(3) Å	$\gamma = 71.066(3)^\circ$
Volume	2125.8(6) Å <sup>3</sup>	
Z	4	
Density (calculated)	1.417 Mg/m <sup>3</sup>	
Absorption coefficient	0.263 mm <sup>-1</sup>	
F(000)	944	
Crystal size	0.33 x 0.18 x 0.11 mm <sup>3</sup>	
Theta range for data collection	1.33 to 27.52°	
Index ranges	-13 ≤ h ≤ 5, -13 ≤ k ≤ 10,	
	-19 ≤ l ≤ 19	
Reflections collected	6552	
Independent reflections	6136 [R(int) = 0.0364]	
Completeness to theta = 27.48°	62.6 %	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F <sup>2</sup>	
Data / restraints / parameters	6136 / 0 / 559	
Goodness-of-fit on F <sup>2</sup>	1.019	
Final R indices [I > 2σ(I)]	R1 = 0.0816, wR2 = 0.2126	
R indices (all data)	R1 = 0.1134, wR2 = 0.2307	
Largest diff. peak and hole	2.993 and -1.094 e.Å <sup>-3</sup>	



**Table S6.** Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for  $[\text{PPh}_4][\text{SO}_3\text{NFH}]$ .  $U(\text{eq})$  is defined as one third of the trace of the orthogonalized  $U^{ij}$  tensor.

	x	y	z	U(eq)
P(1)	5508(1)	1891(1)	1566(1)	18(1)
P(2)	9581(1)	3176(1)	3418(1)	16(1)
S(1)	4745(1)	7171(1)	2424(1)	19(1)
S(2)	9273(2)	7842(2)	2576(1)	46(1)
F(1)	5062(3)	8211(3)	3572(2)	32(1)
F(2)	10421(4)	6800(3)	1487(2)	46(1)
O(1)	5447(4)	6299(3)	3038(2)	26(1)
O(2)	3271(3)	7529(3)	2489(2)	29(1)
O(3)	5186(4)	7139(3)	1540(2)	24(1)
O(4)	9791(5)	7976(4)	3475(2)	43(1)
O(5)	8204(4)	7407(3)	2581(2)	34(1)
O(6)	9085(4)	8715(3)	1918(2)	37(1)
N(1)	5234(4)	8155(4)	2635(3)	22(1)
N(2)	10657(5)	6925(5)	2393(3)	52(2)
C(1)	4716(5)	3216(5)	1512(3)	17(2)
C(2)	5464(6)	3877(6)	1334(3)	23(2)
C(3)	4848(6)	4911(7)	1306(4)	30(2)
C(4)	3485(6)	5288(6)	1471(4)	30(2)
C(5)	2731(6)	4636(6)	1659(4)	28(2)
C(6)	3332(6)	3613(6)	1673(3)	23(2)
C(7)	7060(5)	1663(5)	1001(3)	15(1)
C(8)	8342(5)	1163(5)	1409(3)	23(2)
C(9)	9491(5)	1000(5)	923(3)	25(2)
C(10)	9361(5)	1316(5)	33(3)	23(2)
C(11)	8091(5)	1805(5)	-376(3)	22(2)
C(12)	6937(5)	1982(5)	100(3)	20(2)
C(13)	5830(5)	1309(5)	2682(3)	21(2)
C(14)	6611(6)	295(6)	2885(3)	28(2)
C(15)	6824(6)	-164(6)	3746(4)	35(2)
C(16)	6256(7)	403(7)	4402(4)	41(2)
C(17)	5500(7)	1401(6)	4204(3)	32(2)

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C(18)	5289(6)	1862(5)	3352(3)	28(2)
C(19)	4397(5)	1402(5)	1016(3)	14(2)
C(20)	3671(5)	1955(5)	256(3)	21(2)
C(21)	2937(5)	1522(6)	-235(3)	22(2)
C(22)	2920(5)	567(6)	37(3)	21(2)
C(23)	3629(5)	8(5)	796(3)	22(2)
C(24)	4364(5)	437(6)	1284(3)	21(2)
C(25)	10664(5)	3675(5)	3989(3)	14(2)
C(26)	11308(5)	3136(5)	4776(3)	23(2)
C(27)	12049(5)	3550(6)	5279(4)	28(2)
C(28)	12175(5)	4464(6)	4984(3)	26(2)
C(29)	11551(5)	5005(5)	4198(4)	27(2)
C(30)	10799(5)	4600(5)	3700(3)	20(2)
C(31)	9204(5)	3841(5)	2320(3)	16(2)
C(32)	9647(5)	3301(5)	1614(3)	22(2)
C(33)	9359(6)	3819(6)	776(3)	32(2)
C(34)	8650(6)	4835(6)	637(3)	33(2)
C(35)	8203(5)	5370(5)	1330(3)	26(2)
C(36)	8474(5)	4858(5)	2175(3)	23(2)
C(37)	8028(5)	3328(5)	3975(3)	16(2)
C(38)	6765(5)	3903(5)	3596(3)	19(2)
C(39)	5618(5)	4047(5)	4084(3)	22(2)
C(40)	5739(5)	3621(5)	4947(3)	24(2)
C(41)	7000(5)	3026(5)	5332(3)	24(2)
C(42)	8158(5)	2873(5)	4850(3)	18(2)
C(43)	10452(5)	1859(5)	3413(3)	17(2)
C(44)	9750(6)	1165(6)	3509(3)	24(2)
C(45)	10425(6)	153(6)	3446(4)	32(2)
C(46)	11790(6)	-171(6)	3287(4)	33(2)
C(47)	12495(6)	516(6)	3210(3)	27(2)
C(48)	11844(5)	1526(6)	3267(3)	22(2)

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**Table S7.** Bond lengths [ $\text{\AA}$ ] and angles [ $^\circ$ ] for  $[\text{PPh}_4][\text{SO}_3\text{NFH}]$ .

P(1)-C(1)	1.770(7)	C(16)-C(17)	1.362(9)
P(1)-C(7)	1.791(5)	C(17)-C(18)	1.375(8)
P(1)-C(19)	1.792(5)	C(19)-C(24)	1.378(8)
P(1)-C(13)	1.794(5)	C(19)-C(20)	1.391(7)
P(2)-C(43)	1.783(7)	C(20)-C(21)	1.402(8)
P(2)-C(37)	1.795(5)	C(21)-C(22)	1.360(8)
P(2)-C(25)	1.797(5)	C(22)-C(23)	1.387(8)
P(2)-C(31)	1.804(5)	C(23)-C(24)	1.395(8)
S(1)-O(1)	1.433(4)	C(25)-C(30)	1.372(8)
S(1)-O(3)	1.447(3)	C(25)-C(26)	1.390(7)
S(1)-O(2)	1.457(4)	C(26)-C(27)	1.400(8)
S(1)-N(1)	1.694(5)	C(27)-C(28)	1.354(8)
S(2)-O(5)	1.432(4)	C(28)-C(29)	1.384(8)
S(2)-O(6)	1.448(4)	C(29)-C(30)	1.393(7)
S(2)-O(4)	1.551(4)	C(31)-C(36)	1.374(8)
S(2)-N(2)	1.648(6)	C(31)-C(32)	1.410(7)
F(1)-N(1)	1.473(5)	C(32)-C(33)	1.382(7)
F(2)-N(2)	1.470(6)	C(33)-C(34)	1.368(9)
C(1)-C(2)	1.396(8)	C(34)-C(35)	1.389(9)
C(1)-C(6)	1.399(8)	C(35)-C(36)	1.390(7)
C(2)-C(3)	1.383(9)	C(37)-C(38)	1.381(7)
C(3)-C(4)	1.379(9)	C(37)-C(42)	1.407(7)
C(4)-C(5)	1.392(9)	C(38)-C(39)	1.385(7)
C(5)-C(6)	1.370(9)	C(39)-C(40)	1.379(7)
C(7)-C(8)	1.394(7)	C(40)-C(41)	1.389(8)
C(7)-C(12)	1.401(6)	C(41)-C(42)	1.388(7)
C(8)-C(9)	1.384(7)	C(43)-C(44)	1.390(8)
C(9)-C(10)	1.384(7)	C(43)-C(48)	1.397(7)
C(10)-C(11)	1.382(7)	C(44)-C(45)	1.387(9)
C(11)-C(12)	1.379(7)	C(45)-C(46)	1.376(8)
C(13)-C(14)	1.388(8)	C(46)-C(47)	1.384(9)
C(13)-C(18)	1.393(8)	C(47)-C(48)	1.379(8)
C(14)-C(15)	1.386(7)		
C(15)-C(16)	1.392(9)		

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C(1)-P(1)-C(7)	108.5(3)	C(12)-C(7)-P(1)	116.7(4)
C(1)-P(1)-C(19)	108.2(3)	C(9)-C(8)-C(7)	119.7(5)
C(7)-P(1)-C(19)	108.5(2)	C(8)-C(9)-C(10)	120.0(5)
C(1)-P(1)-C(13)	109.9(3)	C(11)-C(10)-C(9)	120.5(5)
C(7)-P(1)-C(13)	111.1(2)	C(12)-C(11)-C(10)	120.2(5)
C(19)-P(1)-C(13)	110.6(3)	C(11)-C(12)-C(7)	119.6(5)
C(43)-P(2)-C(37)	109.1(3)	C(14)-C(13)-C(18)	119.3(5)
C(43)-P(2)-C(25)	108.0(3)	C(14)-C(13)-P(1)	120.1(4)
C(37)-P(2)-C(25)	109.6(2)	C(18)-C(13)-P(1)	120.6(5)
C(43)-P(2)-C(31)	110.8(3)	C(15)-C(14)-C(13)	120.1(6)
C(37)-P(2)-C(31)	109.8(2)	C(14)-C(15)-C(16)	119.4(7)
C(25)-P(2)-C(31)	109.6(3)	C(17)-C(16)-C(15)	120.5(6)
O(1)-S(1)-O(3)	115.3(2)	C(16)-C(17)-C(18)	120.4(6)
O(1)-S(1)-O(2)	114.4(2)	C(17)-C(18)-C(13)	120.3(7)
O(3)-S(1)-O(2)	114.1(2)	C(24)-C(19)-C(20)	119.3(5)
O(1)-S(1)-N(1)	108.5(2)	C(24)-C(19)-P(1)	120.6(4)
O(3)-S(1)-N(1)	98.0(2)	C(20)-C(19)-P(1)	119.7(5)
O(2)-S(1)-N(1)	104.3(2)	C(19)-C(20)-C(21)	119.8(6)
O(5)-S(2)-O(6)	114.6(3)	C(22)-C(21)-C(20)	120.1(5)
O(5)-S(2)-O(4)	116.6(2)	C(21)-C(22)-C(23)	120.9(5)
O(6)-S(2)-O(4)	113.3(3)	C(22)-C(23)-C(24)	119.1(6)
O(5)-S(2)-N(2)	104.8(3)	C(19)-C(24)-C(23)	120.8(5)
O(6)-S(2)-N(2)	109.4(3)	C(30)-C(25)-C(26)	119.3(5)
O(4)-S(2)-N(2)	95.7(3)	C(30)-C(25)-P(2)	121.9(4)
F(1)-N(1)-S(1)	106.4(3)	C(26)-C(25)-P(2)	118.7(5)
F(2)-N(2)-S(2)	103.1(3)	C(25)-C(26)-C(27)	120.2(6)
C(2)-C(1)-C(6)	119.0(7)	C(28)-C(27)-C(26)	119.8(5)
C(2)-C(1)-P(1)	120.8(5)	C(27)-C(28)-C(29)	120.7(5)
C(6)-C(1)-P(1)	120.2(5)	C(28)-C(29)-C(30)	119.7(6)
C(3)-C(2)-C(1)	120.7(6)	C(25)-C(30)-C(29)	120.4(5)
C(4)-C(3)-C(2)	119.5(6)	C(36)-C(31)-C(32)	120.4(5)
C(3)-C(4)-C(5)	120.4(7)	C(36)-C(31)-P(2)	120.3(4)
C(6)-C(5)-C(4)	120.3(6)	C(32)-C(31)-P(2)	119.2(5)
C(5)-C(6)-C(1)	120.1(6)	C(33)-C(32)-C(31)	118.8(6)
C(8)-C(7)-C(12)	120.0(4)	C(34)-C(33)-C(32)	120.5(6)
C(8)-C(7)-P(1)	123.3(4)	C(33)-C(34)-C(35)	121.0(5)

C(34)-C(35)-C(36)	119.2(6)
C(31)-C(36)-C(35)	120.1(5)
C(38)-C(37)-C(42)	120.5(4)
C(38)-C(37)-P(2)	122.9(4)
C(42)-C(37)-P(2)	116.5(4)
C(37)-C(38)-C(39)	119.8(5)
C(40)-C(39)-C(38)	120.1(5)
C(39)-C(40)-C(41)	120.7(5)
C(42)-C(41)-C(40)	119.8(5)
C(41)-C(42)-C(37)	119.0(5)
C(44)-C(43)-C(48)	119.5(6)
C(44)-C(43)-P(2)	120.8(5)
C(48)-C(43)-P(2)	119.6(5)
C(45)-C(44)-C(43)	120.1(6)
C(46)-C(45)-C(44)	120.4(7)
C(45)-C(46)-C(47)	119.5(7)
C(48)-C(47)-C(46)	121.1(6)
C(47)-C(48)-C(43)	119.4(6)

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**Table S8.** Anisotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for  $[\text{PPh}_4][\text{SO}_3\text{NFH}]$ . The anisotropic displacement factor exponent takes the form:  $-2\pi^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$ .

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{23}$	$U^{13}$	$U^{12}$
P(1)	21(1)	15(2)	18(1)	0(1)	1(1)	-8(1)
P(2)	17(1)	13(2)	16(1)	-1(1)	1(1)	-4(1)
S(1)	21(1)	19(2)	17(1)	-1(1)	1(1)	-6(1)
S(2)	25(1)	49(2)	56(1)	13(1)	-4(1)	-9(1)
F(1)	37(2)	28(3)	32(2)	-13(2)	4(1)	-10(2)
F(2)	67(3)	35(4)	36(2)	-11(2)	-3(2)	-14(2)
O(1)	37(2)	7(4)	27(2)	6(2)	-1(2)	-2(2)
O(2)	23(2)	36(4)	29(2)	-5(2)	4(2)	-11(2)
O(3)	29(2)	21(4)	21(2)	-2(2)	6(2)	-6(2)
O(4)	78(3)	27(4)	17(2)	4(2)	2(2)	-9(3)
O(5)	21(2)	45(4)	37(2)	-8(2)	1(2)	-14(2)
O(6)	44(2)	14(4)	35(2)	21(2)	-1(2)	3(2)
N(1)	36(3)	13(5)	18(2)	7(2)	2(2)	-13(3)
N(2)	33(3)	57(6)	52(3)	17(3)	-5(2)	-4(3)
C(1)	30(3)	0(6)	20(2)	0(2)	0(2)	-4(3)
C(2)	32(3)	8(7)	29(3)	1(3)	-2(2)	-7(4)
C(3)	37(3)	14(8)	41(3)	4(3)	-5(3)	-14(4)
C(4)	44(4)	0(6)	42(3)	-3(3)	-3(3)	0(3)
C(5)	34(3)	15(7)	34(3)	-3(3)	4(2)	-5(4)
C(6)	30(3)	9(7)	30(3)	0(3)	8(2)	-9(3)
C(7)	21(2)	3(5)	23(2)	-2(2)	1(2)	-7(3)
C(8)	28(3)	19(5)	22(3)	-2(3)	-3(2)	-10(3)
C(9)	21(3)	16(6)	34(3)	-1(3)	-3(2)	-2(3)
C(10)	22(3)	17(5)	29(3)	-5(3)	8(2)	-5(3)
C(11)	30(3)	15(5)	22(3)	-2(3)	4(2)	-10(3)
C(12)	23(3)	11(5)	24(3)	5(3)	0(2)	-8(3)
C(13)	23(3)	14(6)	23(3)	2(3)	-2(2)	-7(3)
C(14)	30(3)	35(7)	23(3)	-4(3)	0(2)	-18(4)
C(15)	32(3)	29(6)	39(3)	18(3)	-8(3)	-13(3)
C(16)	54(4)	58(8)	20(3)	10(4)	-4(3)	-36(5)
C(17)	56(4)	26(7)	23(3)	-7(3)	5(3)	-25(4)
C(18)	35(3)	25(6)	26(3)	-1(3)	1(2)	-16(3)

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C(19)	18(3)	4(6)	19(2)	3(3)	1(2)	-5(3)
C(20)	23(3)	9(5)	31(3)	3(3)	-2(2)	-8(3)
C(21)	24(3)	10(7)	31(3)	-1(3)	-4(2)	-4(3)
C(22)	18(3)	11(6)	36(3)	-10(3)	0(2)	-6(3)
C(23)	29(3)	10(5)	29(3)	-4(3)	5(2)	-8(3)
C(24)	22(3)	16(7)	23(3)	-6(3)	3(2)	-2(3)
C(25)	18(2)	1(6)	19(2)	3(2)	2(2)	-2(3)
C(26)	27(3)	18(5)	24(3)	5(3)	-2(2)	-9(3)
C(27)	26(3)	27(7)	29(3)	0(3)	-2(2)	-8(3)
C(28)	20(3)	25(7)	32(3)	-15(3)	0(2)	-4(3)
C(29)	32(3)	11(6)	41(3)	-5(3)	-2(2)	-10(3)
C(30)	24(3)	11(6)	23(3)	-1(3)	-1(2)	-2(3)
C(31)	19(3)	10(6)	17(2)	1(2)	-1(2)	-2(3)
C(32)	26(3)	17(5)	21(3)	-2(3)	2(2)	-6(3)
C(33)	39(3)	34(7)	21(3)	0(3)	3(2)	-9(4)
C(34)	35(3)	41(7)	19(3)	13(3)	-6(2)	-13(4)
C(35)	26(3)	14(6)	31(3)	12(3)	-3(2)	-2(3)
C(36)	23(3)	21(7)	26(3)	-1(3)	2(2)	-6(3)
C(37)	23(3)	8(5)	20(2)	-6(2)	5(2)	-7(3)
C(38)	21(3)	11(5)	24(3)	-3(3)	0(2)	-5(3)
C(39)	18(3)	13(5)	33(3)	-3(3)	1(2)	-2(3)
C(40)	25(3)	19(6)	32(3)	-8(3)	11(2)	-10(3)
C(41)	30(3)	22(6)	21(2)	-2(3)	7(2)	-9(3)
C(42)	25(3)	10(5)	20(2)	-2(2)	2(2)	-5(3)
C(43)	27(3)	5(5)	16(2)	-3(2)	2(2)	0(3)
C(44)	28(3)	14(7)	27(3)	-2(3)	-3(2)	-5(4)
C(45)	41(4)	15(7)	39(3)	-4(3)	-8(3)	-10(4)
C(46)	44(4)	12(6)	34(3)	-7(3)	-7(3)	5(4)
C(47)	30(3)	13(7)	26(3)	0(3)	6(2)	7(4)
C(48)	28(3)	7(6)	25(3)	1(3)	5(2)	0(3)

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